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NUCLEAR MAGNETIC RESONANCE (NMR)

Nuclear magnetic resonance (NMR) can be used like IR to help identify samples. But if you thought the instrumentation for IR was complicated, these NMR instruments are even worse. So I'll only give some generalities and directions for preparing samples.

For organic lab, traditionally you look only at the signals from protons in your compound; sometimes then, this technique is called **proton magnetic resonance (PMR)**. Not naked H^+ protons either, eh? The everyday **hydrogens** in organic compounds are just called **protons** when you use this technique.

A sample in a special tube is spun between the poles of a strong magnet. A radio-frequency signal, commonly 60 MHz, a little higher than TV Channel 2, is applied to the sample. Now, if *all* protons were in the same environment, there'd be this big absorption of energy in one place in the PMR spectrum. Big deal. But all protons are *not* the same. If they're closer to electronegative groups, or on aromatic rings, the signals shift to a different frequency. This change in the position of the PMR signals, which depends on the chemistry of the molecule, is called the **chemical shift**. Thus, you can tell quite a bit about a compound if you have its NMR.

LIQUID SAMPLE PREPARATION

To prepare a liquid sample for NMR analysis,

1. Get an **NMR tube**. These tubes are about 180 mm long and 5 mm wide, and the cost is about a buck apiece for what is euphemistically called the inexpensive model. The tubes are not precision ground, and some may stick in the NMR probe. This should not be your worry, though. They also have matching, color-coordinated designer caps (Fig. 169).
2. Get a **disposable pipet** and a little **rubber bulb** and construct a **narrow medicine dropper**. Use this to transfer your sample to the NMR tube. Don't fill it much higher than about 3–4 cm. Without any solvent, this is called, of course, a **neat sample**.
3. Ask about an **internal standard**. Usually **tetramethylsilane (TMS)** is chosen because most other proton signals from any sample you might have fall at *lower frequencies* than that of the protons in TMS. Sometimes **hexamethyldisiloxane (HMDS)** is used because it

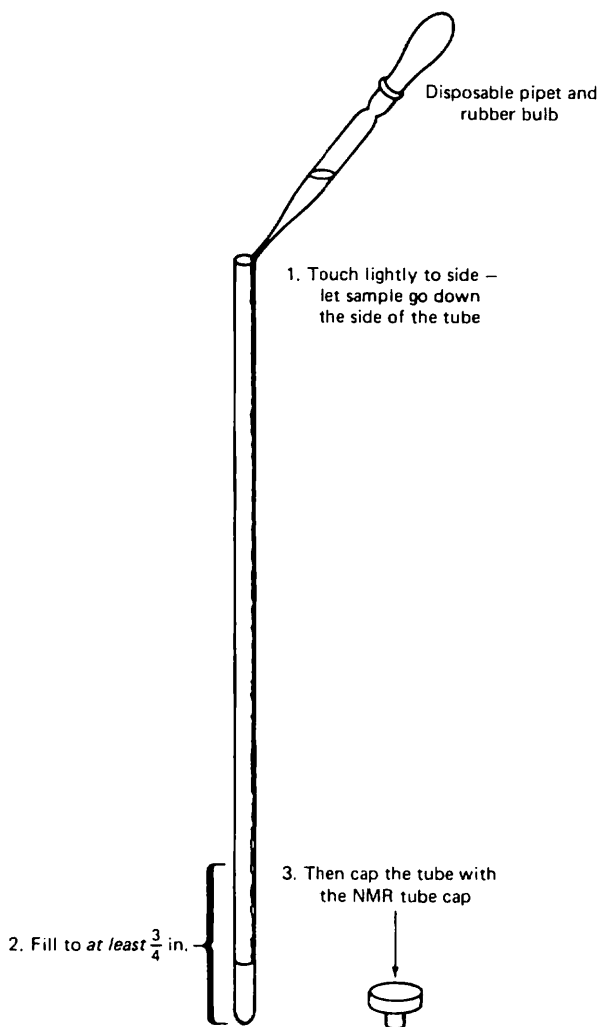


Fig. 169 Loading the typical NMR tube.

doesn't boil out of the NMR tube like TMS can. TMS boils at 26–28°C; HMDS boils at 101°C. Add *only* one or two drops.

4. Cap the tube and have the NMR of the sample taken. It's really out of place for me to tell you more about NMR here. Buy my next book, *If They Don't Work...They're Machines*.
5. Last point: cleanliness. If there is *trash* in the sample, get rid of it. Filter it or something, will you?

SOLID SAMPLES

Lucky you. You have a solid instead of a liquid. This presents one problem. What are you going to dissolve the solid in? Once it's a solution, you handle it just like a **liquid sample**. Unfortunately, if the *solvent has protons* and you know there'll be much more solvent than sample, you'll get a major proton signal from your solvent. Not a good thing, especially if the signals from your solvent and sample overlap.

Protonless Solvents

Carbon tetrachloride, a solvent without protons, is a typical protonless solvent. In fact, it's practically the only example. So if your sample dissolves in CCl_4 , you're golden. Get at least 100 mg of your compound in enough solvent to fill the NMR tube to the proper height.

Caution! CCl_4 is toxic and potentially carcinogenic. Handle with *extreme care*.

Deuterated Solvents

If your compound does not happen to dissolve in CCl_4 , you still have a shot because *deuterium atoms do not give PMR signals*. This is logical, since they're not protons. The problem is that *deuterated solvents are expensive*, so do NOT ask for, say D_2O or CDCl_3 , the **deuterated analogs of water** and **chloroform**, unless you're absolutely sure your compound will dissolve in them. Always use the protonic solvent— H_2O or CHCl_3 here—for the solubility test. There are other deuterated solvents, and they may or may not be available for use. Check with your instructor.

SOME NMR INTERPRETATION

I've included a spectrum of ethylbenzene (Fig. 170) to give you some idea of how to start interpreting NMRs. Obviously, you'll need more than this. See your instructor or any good organic chemistry text for more information.

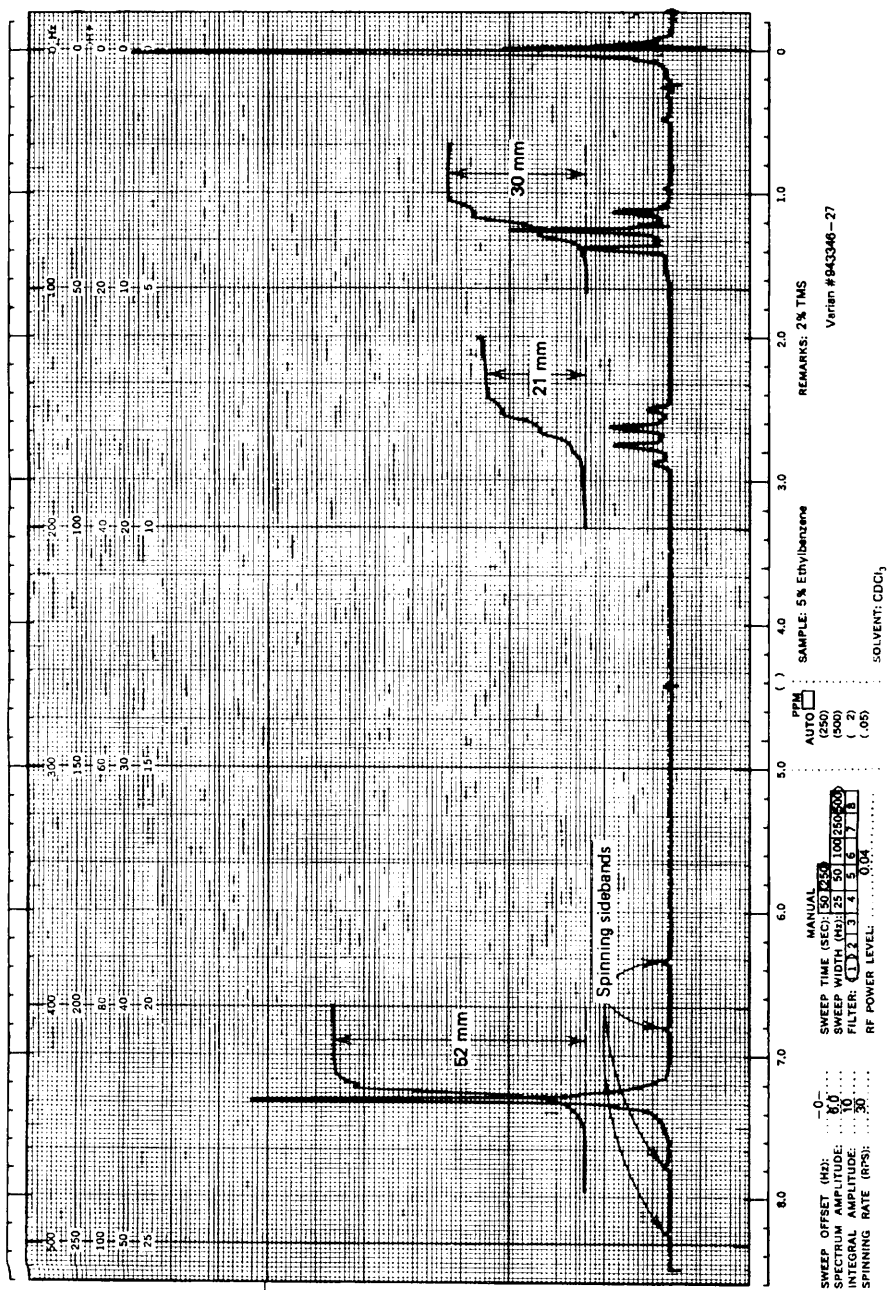


Fig. 170 NMR of ethylbenzene.

The Zero Point

Look at the extreme right of the NMR. That single, sharp peak comes from the protons in the **internal standard**, TMS. This signal is *defined as zero*, and all other values for the **chemical shift** are taken from this point. The units are parts per million (ppm) and use the Greek letter delta δ : $\delta 0.0$.

Protons of almost all other compounds you'll see will give signals *to the left of zero*; positive δ values, **shifted downfield** from TMS. There are compounds that give PMR signals **shifted upfield** from TMS: negative δ values.

Upfield and downfield are directions relative to where you point your finger on the NMR chart. Signals to the *right* of where you are: **upfield**. Signals to the *left* of where you are: **downfield**.

The Chemical Shift

You can see that not all the peaks fall in the same place, so the protons must be in different surroundings. There is one signal at $\delta 1.23$, one at $\delta 2.75$, and another at $\delta 7.34$. You usually take these values from the *center* of a **split signal** (that's coming up). See that the TMS is really zero before you report the chemical shift. If it is not at zero, you'll have to add or subtract one correction to all the values. This is the same as using a polystyrene calibration peak to get an accurate fix on IR peaks.

You'll need a correlation table or a correlation chart (Fig. 171) to help interpret your spectrum. The $-\text{CH}_3$ group is about in the right place ($\delta 1.23$). The $\delta 7.34$ signal is from the aromatic ring, and, sure enough, that's where signals from aromatic rings fall. The $\delta 2.75$ signal from the $-\text{CH}_2-$ is a bit trickier to interpret. The chart shows a $-\text{CH}_3$ on a benzene ring in this area. Don't be literal and argue that *you don't have a* $-\text{CH}_3$; you have a $-\text{CH}_2-\text{CH}_3$. All right, they're different. But the $-\text{CH}_2-$ group *is on a benzene ring and attached to a* $-\text{CH}_3$. That's why those $-\text{CH}_2$ protons are further downfield; that's why you don't classify them with ordinary $\text{R}-\text{CH}_2-\text{R}$ protons. Use some sense and judgment.

I've blocked out related groups on the correlation table. Look at the set from $\delta 3.1$ to $\delta 4.0$. They're the area that protons on carbons attached to halogens fall in. Read that again. It's protons on *carbons* attached to halogens. The more electronegative the halogen on the carbon, the further *downfield* the *chemical shift* of those protons. The electronegative halogen

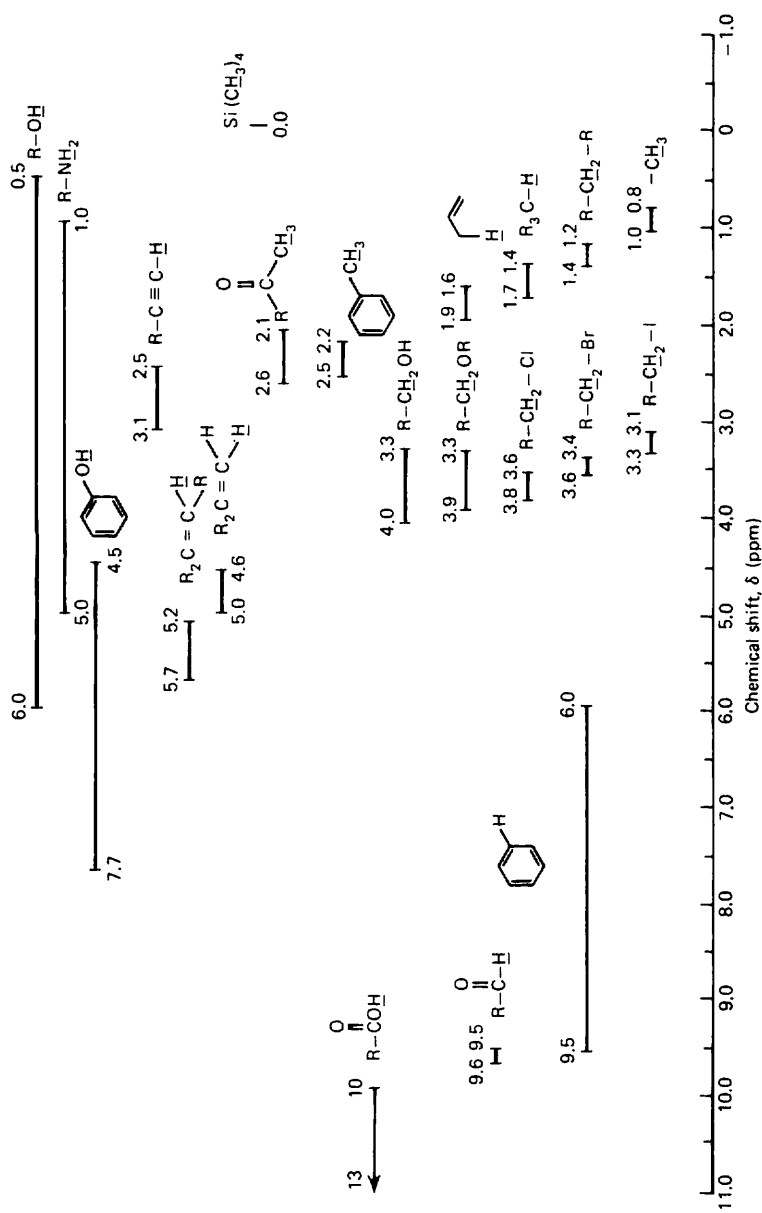


Fig. 171 A garden variety NMR correlation chart.

draws electrons from the carbon and thus from around the protons on the carbon. These protons now don't have as many electrons surrounding them. They are *not as shielded* from the big bad magnetic field as they might be. They are **deshielded**, so their signal falls *downfield*.

The hydrogen-bonded protons wander all over the lot. Where you find them, and how sharp their signals are, depend at least on the solvent, the concentration, and the temperature.

Some Anisotropy

So what about aromatic protons ($\delta 6.0$ – 9.5), aldehyde protons ($\delta 5$ – 9.6), or even protons on double, nay triple, bonds ($\delta 5$ – 3.1)? All these protons are attached to carbons with π bonds, double or triple bonds, or aromatic systems. The electrons in these π bonds *generate their own little local magnetic field*. This local field is not *spherically symmetric*; it can shield or deshield protons depending on where the protons are—it's **anisotropic**. In Fig. 172, the **shielding regions** have pluses on them, and **deshielding regions** have minuses.

This is one of the quirks in the numbering system. Physically and psychosocially, a minus means *less (less shielding)*, and DOWNfield is further left on the paper; yet the value of δ goes UP. Another system uses

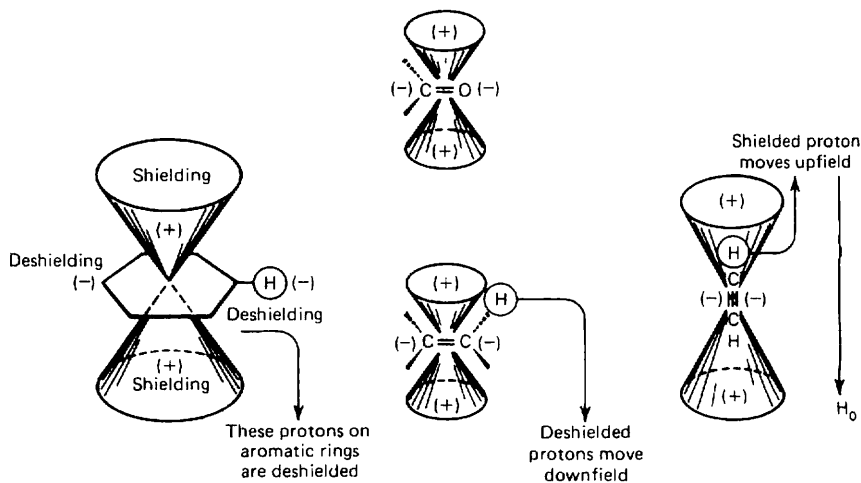


Fig. 172 Anisotropic local magnetic fields on display.

the Greek tau (τ)—that's 10.0– δ . So δ 0.00 (ppm) is 10.0 τ . Don't confuse these two systems. And don't ever confuse deshielding (or shielding) with the *proper direction of the chemical shift*.

Spin-Spin Splitting

Back to ethylbenzene. You'll find that the $\text{—CH}_2\text{—}$ and the CH_3 protons are not single lines; they are *split*. **Spin-spin splitting**. Such a fancy name. Protons have a spin of plus or minus $\frac{1}{2}$. If I'm sitting on the methyl group, I can see two protons on the adjacent carbon ($\text{—CH}_2\text{—}$). (**Adjacent carbon**, remember that.) They spin, so they produce a magnetic field. Which way do they spin? That's the crucial point. Both can spin one way, *plus*. Both can spin one way, *minus*. Or, each can go a different way; one plus, one minus.

Over at the methyl group (**adjacent carbon**, eh?), you can feel these fields. They add a little, they subtract a little, they cancel a little. So your methyl group splits into three peaks! It's split by the *two protons on the adjacent carbon*.

Don't confuse this with the fact that there are three protons on the methyl group! That Has Nothing To DO With It! It is mere coincidence.

The methyl group shows up as a **triplet** because it is split by *two* protons on the *adjacent carbon*.

Now what about the intensities? Why is the middle peak larger? Get out a marker and draw an A on one proton and a B on the other. OK. There's only one way for A and B to spin in the same direction: *Both A and B are plus*, or *both A and B are minus*. But there are *two ways* for them to spin opposite each other: *A plus with B minus*; *B plus with A minus*. This condition happens *two times*. Both A and B plus happen only *one time*. Both A and B minus happen only *one time*. So what? So the **ratio of the intensities is 1:2:1**. Ha! You got it—a **triplet**. Do this whole business sitting on the $\text{—CH}_2\text{—}$ group. You get a **quartet**—*four lines*—*because the $\text{—CH}_2\text{—}$ protons are adjacent to a methyl group*. They are split BY *three* to give *FOUR* lines (Fig. 173).

No, that is not all. You can tell that the $\text{—CH}_2\text{—}$ protons and the —CH_3 protons split each other by their **coupling constant**, the distance between the split peaks of a single group. Coupling constants are called **J values** and are usually given in hertz (Hz). You can read them right from the chart, which has a grid calibrated in hertz. If you find protons at different

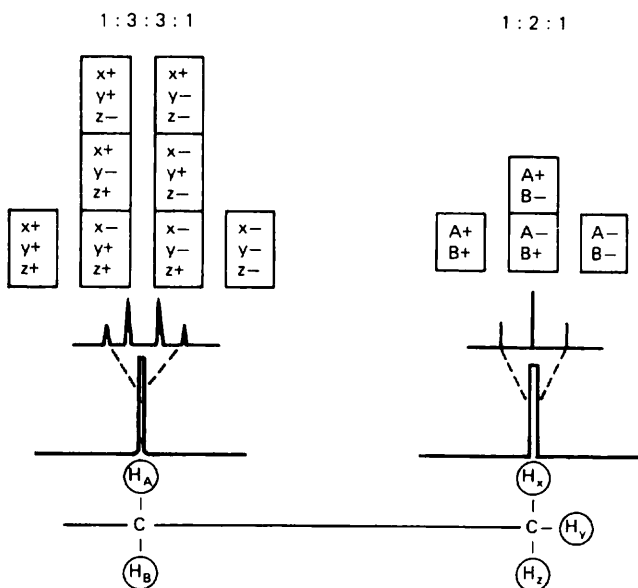


Fig. 173 Spin alignments for the ethyl group.

chemical shifts and their coupling constants are the same, they're splitting and coupling with each other.

Integration

Have you wondered about those funny curves drawn over the NMR peaks? They're **electronic integrations**, and they can tell you how many protons there are at each chemical shift. Measure the distances between the horizontal lines just before and just after each group. With a cheap plastic ruler, I get 52 mm for the benzene ring protons, 21 mm for the $-CH_2-$ protons, and about 30 mm for the $-CH_3$ protons. Now you divide all the values by the smallest one. Well, 21 mm is the smallest, and without a calculator I get 2.47:1:1.43. Not even close. And how do you get that 0.47 or 0.43 proton? Try for the simplest *whole number ratio*. Multiply everything by 2, and you'll have 4.94:2:2.86. This is very close to 5:2:3, the actual number of protons in ethylbenzene. Use other whole numbers; the results are not as good, and you can't justify the splitting pattern—3 *split* BY 2 and 2 *split* BY 3—with other ratios. Don't use each piece of information in a vacuum.

There are a lot of other things in a typical NMR. There are **spinning sidebands**, small duplicates of stronger peaks, evenly spaced from the parent peak. They fall at *multiples of the spin rate*, which here is about 30 Hz. Spin the sample tube faster and these sidebands move farther away; slow the tube and they must get closer.

Signals that split each other tend to lean toward each other. It's really noticeable in the triplet and even distorts the intensity ratio in the quartet somewhat. Ask your instructor or see another textbook if you have questions.